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14. ABSTRACT The intelligent design of lubricants that perform under extreme environments, such as arctic or space conditions, requires an understanding of the how the tribological properties are related to the molecular structure of the lubricant. The purpose of this grant was to understand the relationship between molecular-level perfluoropolyether (PFPE) lubricant architecture and its resulting properties of tribological relevance, including rheological properties and chemical stability. We synthesized a series of PFPE lubricants varying key architectural elements. We characterized the rheological properties of the experimentally synthesized lubricants. We performed non-equilibrium molecular dynamics (NEMD) simulation to model the rheological properties and to understand the fundamental mechanisms governing the relationship between molecular structure and viscosity. We furthermore performed a multiscale suite of simulations combining quantum mechanical (QM) calculations of the reaction rate constants and reactive molecular dynamics (RMD) to model the chemical stability of the components as a function of architecture.					
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**Computational and Experimental Study of High-Performance Lubricants in
Extreme Environments**

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Table of Contents

I. Accomplishments	3
II. Publications	3
III. Presentations	4
IV. Summary of Work	5
IV.A. The Big Picture	5
IV.B. Rheological Properties	5
IV.B.1. The Experimental Standard	6
IV.B.2. Non-equilibrium Molecular Dynamics Simulation	7
IV.C. Chemical Stability	8
IV.C.1. The Quantum Mechanical Standard	9
IV.C.2. Reactive Molecular Dynamics Simulation	10
V. Key Findings	11

I. Accomplishments:

The intelligent design of lubricants that perform under extreme environments, such as arctic or space conditions, requires an understanding of how the tribological properties are related to the molecular structure of the lubricant. The purpose of this grant was to understand the relationship between molecular-level perfluoropolyether (PFPE) lubricant architecture and its resulting properties of tribological relevance, including rheological properties and chemical stability. We synthesized a series of PFPE lubricants varying key architectural elements. We characterized the rheological properties of the experimentally synthesized lubricants. We performed non-equilibrium molecular dynamics (NEMD) simulation to model the rheological properties and to understand the fundamental mechanisms governing the relationship between molecular structure and viscosity. We furthermore performed a multiscale suite of simulations combining quantum mechanical (QM) calculations of the reaction rate constants and reactive molecular dynamics (RMD) to model the chemical stability of the components as a function of architecture.

II. Publications acknowledging this grant for support:

Jiang, B., Keffer, D.J., Edwards, B.J., "A Coarse-Grained Reactive Molecular Dynamics Study of the Thermal Decomposition of CF_3OCF_3 ", *J. Chem. Phys.*, under review, 06/2008.

Jiang, B., Kim, J.M., Keffer, D.J., Edwards, B.J., "Comparison of perfluoropolyethers and n-alkanes under shear via nonequilibrium molecular dynamics simulation", *Mol. Sim.* **34**(2) 2008 pp. 231-242.

Jiang, B., Keffer, D.J., Edwards, B.J., "A quantum mechanical study of the decomposition of CF_3OCF_3 and $\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_3$ in the presence of AlF_3 ", *J. Phys. Chem. A* **112**(12) 2008 pp. 2604-2609.

Jiang, B., Crawford, N.J., Keffer, D.J., Edwards, B.J., Adcock, J.L., "Comparison of rheological properties of short-chain perfluoropolyethers through simulation and experiment", *Mol. Sim.* **33**(9/10) 2007 p. 881-888.

Jiang, B., Keffer, D.J., Edwards, B.J., "Estimation and Analysis of the Rheological Properties of a Perfluoropolyether through Molecular Dynamics Simulation", *J. Fluorine Chem.* **127** 2006 p. 787-795.

III. Presentations at Professional Conferences and Workshops:

Jiang, B. (speaker), Edwards, B.J., Keffer, D.J., "Reactive Molecular Dynamics of the thermal decomposition of CF_3OCF_3 ", AIChE Annual Meeting, Salt Lake City, UT, November, 2007.

Jiang, B. (speaker), Edwards, B.J., Keffer, D.J., "Quantum Mechanics Study of decomposition of CF_3OCF_3 and $(\text{CF}_3\text{CF}_2)_2\text{O}$ catalyzed by AlF_3 ", AIChE Annual Meeting, Salt Lake City, UT, November, 2007.

Jiang, B. (speaker), Adcock, J.L., Crawford, N.J., Fern, J.T., Pangloli, A.F., Edwards, B.J., Steele, W.V., Keffer, D.J., "Understanding the relationship between molecular architecture and thermophysical and rheological properties of perfluoropolyethers", AIChE Annual Meeting, Salt Lake City, UT, November, 2007.

Jiang, B. (speaker), Keffer, D.J., Edwards, B.J., "Estimation and Analysis of the Rheological Properties of Perfluoropolyethers", AIChE Annual Meeting, San Francisco, CA, November, 2006.

Keffer, D.J., "*Computational and Experimental Study of High-Performance Lubricants in Extreme Environments*", AFOSR Tribology Program Review Meeting, University of Florida, Gainesville, FL, November, 2007.

Keffer, D.J., "*Computational and Experimental Study of High-Performance Lubricants in Extreme Environments*", AFOSR Tribology Program Review Meeting, Air Force Research Lab, Dayton, OH, August, 2006.

Keffer, D.J., "*Computational and Experimental Study of High-Performance Lubricants in Extreme Environments*", AFOSR Tribology Program Review Meeting, North Carolina State University, Raleigh, NC, October, 2005.

IV. Summary of Work

IV.A. The Big Picture

The intelligent design of lubricants that perform under extreme environments, such as arctic or space conditions, requires an understanding of how the tribological properties are related to the molecular structure of the lubricant. The goal of this work was to develop insight into the fundamental molecular-level mechanisms governing the relationship between molecular structure of a PFPE lubricant and its (i) rheological properties and (ii) chemical stability. To accomplish this task, we performed appropriate molecular dynamics (MD) simulations and compared them to an appropriate standard. For the rheological properties, we used non-equilibrium molecular dynamics (NEMD) to simulate the PFPE lubricants under flow. The standard that we compared to was the experimental characterization of the lubricants synthesized by Prof. Jamie Adcock. For the chemical stability, we used reactive molecular dynamics (RMD) to simulate the thermal and catalytic decomposition of model PFPE compounds. The standard that we compared to was quantum mechanical calculations. This process is schematically illustrated in Figure 1.

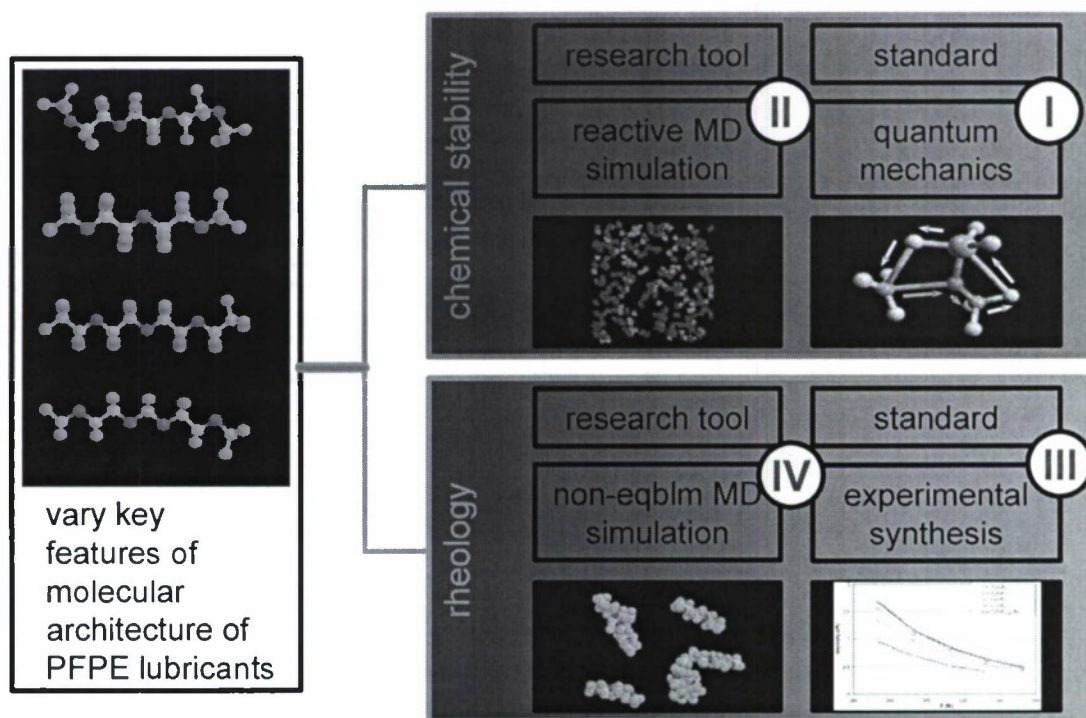
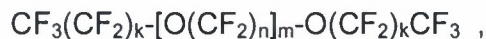


Figure 1. A schematic illustrating the overall methodology used in this grant.

IV.B. Rheological Properties

We studied seven PFPE compounds to establish the relationship between molecular structure and viscosity. The structures of the seven PFPE compounds are summarized in Table 1. All PFPE compounds, except compound 4, can be represented as variations of the generic structure



where m represents the number of monomeric units in the chain, n is the number of CF_2 units in each monomer, and k is the number of CF_2 units in each end group. Thus, m quantifies the chain length, n quantifies the monomer size, and k determines the size of the functional end group. In this study, m assumes values of 2, 3, 5 and 7, n assumes values of 1, 2 and 3, and k assumes values of 0 and 1. Compound 4 is a variation of compound 2, in which an $-\text{OCF}_2-$ monomer has been inserted into the middle of the chain.

These compounds represent variations in key architectural elements including the size of the monomer unit, the size of the end group, and the chain length.

#	chemical formula	structure	backbone atoms	architectural elements
1	$\text{C}_8\text{O}_4\text{F}_{18}$	$\text{CF}_3\text{--}[\text{O}(\text{CF}_2)_2]_3\text{--OCF}_3$	12	base ($m=3$)
2	$\text{C}_6\text{O}_3\text{F}_{14}$	$\text{CF}_3\text{--}[\text{O}(\text{CF}_2)_2]_2\text{--OCF}_3$	9	chain length ($m=2$)
3	$\text{C}_8\text{O}_3\text{F}_{18}$	$\text{CF}_3\text{CF}_2\text{--}[\text{O}(\text{CF}_2)_2]_2\text{--O CF}_2\text{CF}_3$	11	end group
4	$\text{C}_7\text{O}_4\text{F}_{16}$	$\text{CF}_3\text{O}(\text{CF}_2)_2\text{OCF}_2\text{O}(\text{CF}_2)_2\text{OCF}_3$	11	OCF_2O
5	$\text{C}_8\text{O}_3\text{F}_{16}$	$\text{CF}_3\text{--}[\text{O}(\text{CF}_2)_3]_2\text{--OCF}_3$	11	$\text{OC}_3\text{F}_6\text{O}$
6	$\text{C}_{12}\text{O}_6\text{F}_{26}$	$\text{CF}_3\text{--}[\text{O}(\text{CF}_2)_2]_5\text{--OCF}_3$	18	chain length ($m=5$)
7	$\text{C}_{16}\text{O}_8\text{F}_{34}$	$\text{CF}_3\text{--}[\text{O}(\text{CF}_2)_2]_7\text{--OCF}_3$	24	chain length ($m=7$)

Table 1. Summary of PFPE structures and architectural elements.

IV.B.1. The Experimental Standard

In the Chemistry Department at the University of Tennessee, Prof. Jamie Adcock led the team that experimentally synthesized the PFPEs. Viscosities were measured in the Chemical Engineering Department. In Table 2., we report the experimentally measured viscosities as a function of temperature and architecture. These viscosities formed the standard by which the subsequent NEMD simulations were compared.

No.\T (K)	273	293	313	333	353
1	1.68	1.16 (1.18)	0.85	0.64 (0.66)	0.50
2	0.96	0.70 (0.67)	0.52	0.41 (0.43)	-
3	1.56	1.10 (1.06)	0.80	0.61 (0.62)	0.47
4	1.34	0.96 (0.93)	0.71	0.55 (0.53)	0.43
5	1.69	1.16 (1.15)	0.84	0.64 (0.64)	0.49

Table 2. The zero-shear-rate viscosities (cP) at various temperatures for five compounds. The viscosities from NEMD simulations using the revised UFF potential are in parenthesis.

IV.B.2. Non-equilibrium Molecular Dynamics Simulation

In order to elucidate the molecular-level mechanisms responsible for the relationship between PFPE structure and viscosity, we performed NEMD simulations of the PFPEs under flow. There was no interaction potential in the literature capable of correctly reproducing the experimental viscosities. Therefore, we developed and parameterized a new interaction potential which treated the fluorine atoms differently depending upon their local environment. With this revised potential, we were able to achieve an excellent agreement between simulation and experiment, as shown in Figure 2.

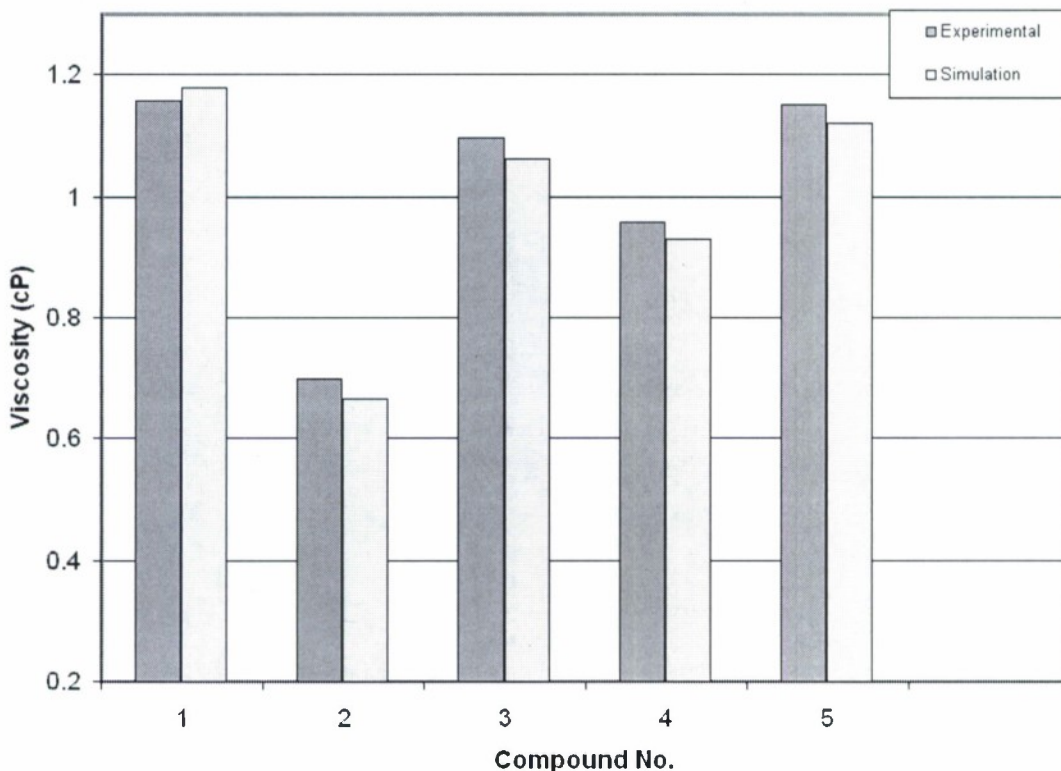


Figure 2. Comparison of experimental and simulated zero-shear rate viscosities as a function of lubricant structure.

By measuring the viscosity of PFPE with different architectural elements both experimentally and in simulation, we can arrive at several general statements regarding the relationship between viscosity and PFPE architecture. First, longer chain backbone lengths increase the viscosity. Second, ether linkages in the backbone decrease the viscosity. Third, longer $(\text{CF}_2)_n$ units between ether linkages increase the viscosity. These effects can all be explained in terms of chain flexibility. The large fluorine atoms create a relatively high-energy barrier for torsional motion required to change from a gauche to trans conformations. The presence of the oxygen significantly reduces this energy barrier. The strategic placement of oxygen in the chain backbone defines the size of the monomeric units and results in the ability to control of the viscosity of compounds that have the same chemical formula.

Additionally, we reported the structural and rheological properties of four short-chain PFPEs with common monomeric units but of varying chain length using NEMD simulation of planar Couette flow. We found a power-law index relating viscosity to chain length of 2, which is generally characteristic of rigid chain molecules. From the alignment angle, we observed that longer chains align to a greater degree in shear flow, as expected. We also saw that longer chains have a more pronounced maximum in the end-to-end distance as a function of shear rate, indicating that longer chains are capable of greater extension (increasing the end-to-end distance at low shear rates) and are more susceptible to rotational phenomena (decreasing the average end-to-end distance at high shear rates). These observations are commensurate with the conceptual understanding that longer chains have a greater relative flexibility.

Finally, we provided a quantitative comparison of the structural and energetic properties of relatively rigid PFPEs and relatively flexible alkanes as functions of chain length. From the end-to-end distance, we found that following the same argument regarding chain flexibility, alkanes show a more pronounced maximum in the end-to-end distance as a function of shear rate. From the alignment angle, we observed that the rigid PFPEs align to a greater extent than flexible alkanes, which also is reasonable based on arguments of relative chain flexibility.

IV.C. Chemical Stability

PFPEs degrade according to two mechanisms: thermal decomposition and catalytic decomposition as shown in Figure 3. Both reactions involve scission of the ether linkage in the backbone. In the catalytic decomposition, residual fluorine byproduct in the lubricant can react with an aluminum or iron surface to form AlF_3 or FeF_3 , which catalytically decomposes the lubricant.

We examined two model perfluorinated ether compounds, as shown in Figure 4, to understand the role of chemical stability relative to the local environment of the ether linkage.

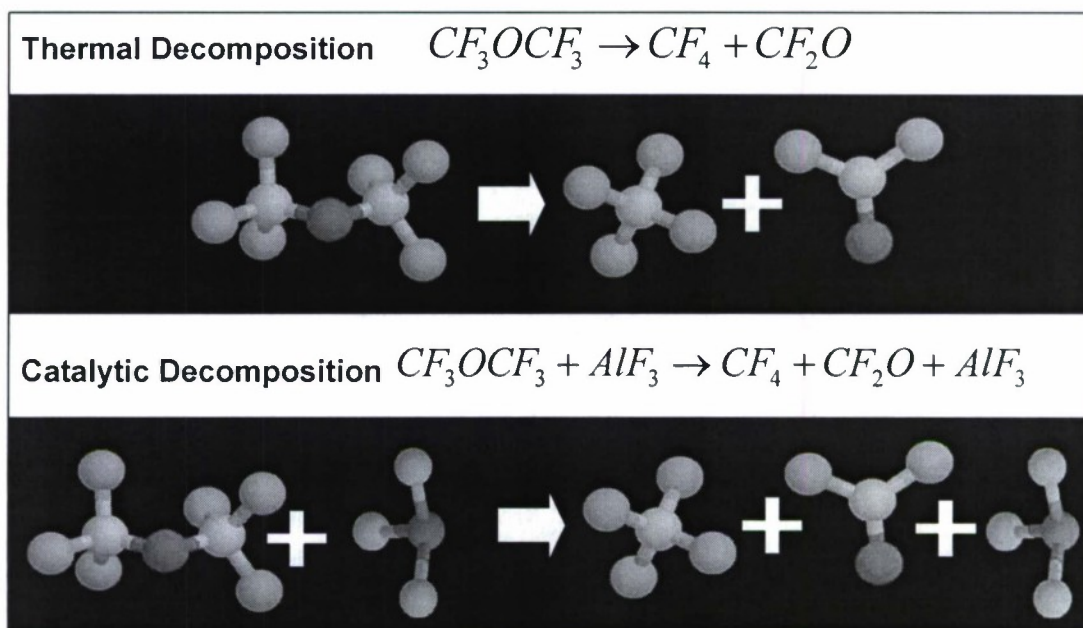


Figure 3. Thermal and catalytic decomposition of perfluorinated ethers. color legend: F-gold, C-gray, O-red, Al-green.

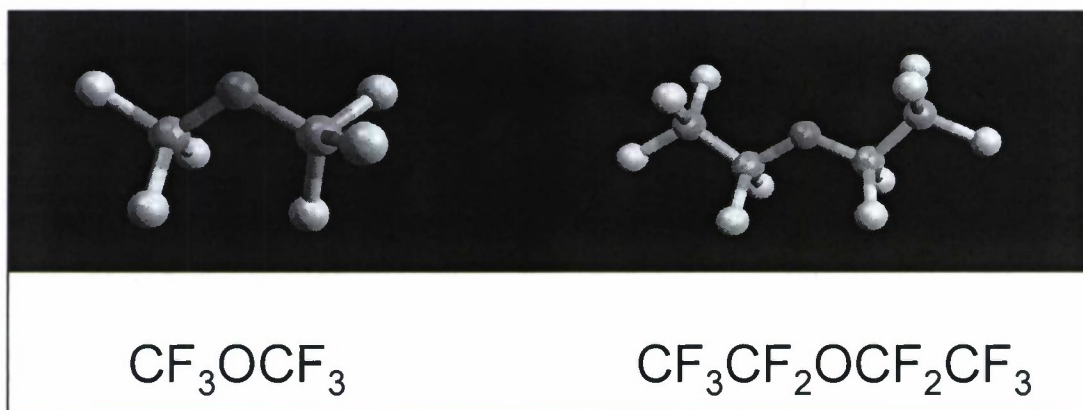


Figure 4. Model perfluorinated ethers. color legend: F-blue, C-gray, O-red.

IV.C.1. The Quantum Mechanical Standard

In the absence of experimental data, we performed quantum mechanical calculations and coupled it with transition state theory to compute the reaction rate for decomposition. We found a qualitatively different mechanism for the catalytic decomposition of the PFPEs than was given in the literature. The old and new transition states are shown in Figure 5.

Using this new transition state, we calculate new reaction rates, as given in Table 3. These new rates show that at room temperature, the catalytic decomposition of these compounds can be 30,000 to 100,000 times faster than was previously thought. Thus, controlling the chemical resistance to catalytic decomposition is critical.

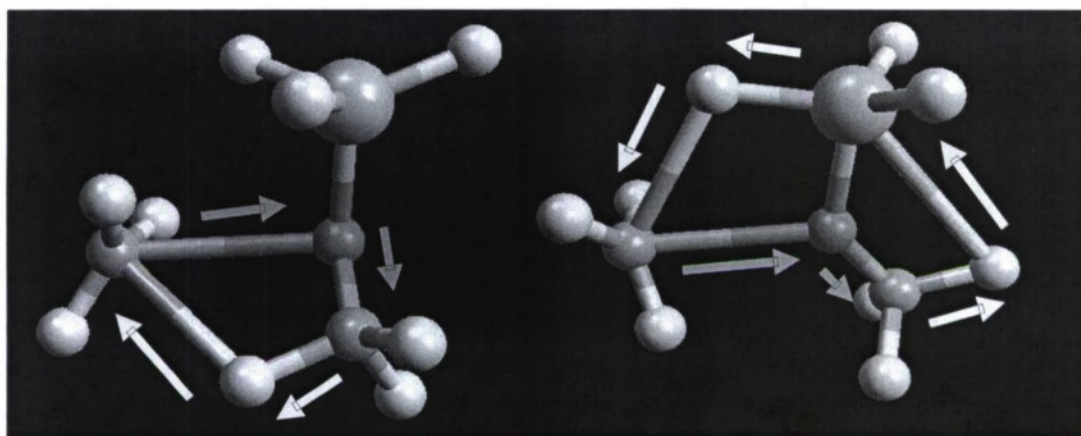


Figure 5. Left: the old transition state in which the AlF_3 simply stabilizes the O. The new transition state in which the AlF_3 actively participates in the reaction as a fluorine transfer agent.

compound	transition state	$k_0(\text{s}^{-1}) \cdot 10^{-14}$	E_a (kJ/mol)
$\text{C}_2\text{F}_6\text{O}$	old	1.6	228
$\text{C}_2\text{F}_6\text{O}$	new	3.5	199
$\text{C}_4\text{F}_{10}\text{O}$	old	0.79	197
$\text{C}_4\text{F}_{10}\text{O}$	new	2.4	172

Table 3. Reaction rate constants for the old and new transition states.

IV.C.2. Reactive Molecular Dynamics Simulation

We developed a coarse-grained reactive molecular dynamics (RMD) simulation technique that allowed us to match the quantum mechanical reaction rates for thermal decomposition in a large MD simulation. This new RMD algorithm demonstrates that we can correctly reproduce quantum mechanical reaction rates using a coarse-grained classical RMD algorithm. This will allow us, in future work, to simulated reaction under flow for dense systems, which is not otherwise possible. A comparison of the parameterized RMD reaction rate and the QM reaction rate is shown in Figure 6.

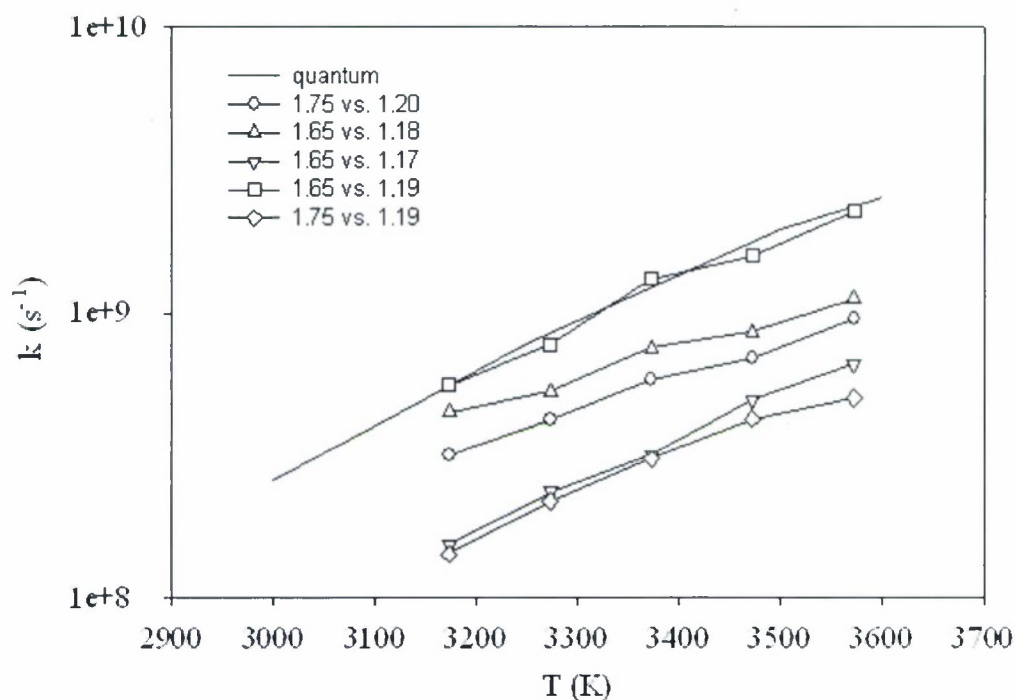


Figure 6. Comparison of the reaction rate as a function of temperature for the quantum mechanical standard and various parameterizations of the coarse-grained reaction molecular dynamics simulation.

V. Key Findings

The key findings in this work are as follows

- Five PFPE lubricants were synthesized and viscosities are reported.
- A new interaction potential for PFPE lubricants was developed.
- The following statements regarding the relationship between PFPE structure and viscosity were validated.

First, longer chain backbone lengths increase the viscosity.

Second, ether linkages in the backbone decrease the viscosity.

Third, longer $(CF_2)_n$ units between ether linkages increase the viscosity.

These effects can all be explained in terms of chain flexibility.

- A new transition state for the catalytic decomposition of PFPEs was discovered, that shows that the decomposition rate can be 100,000 times faster at room temperature than what was previously reported in the literature.
- A new reactive molecular dynamics algorithm was developed that will allow for the reliable and computationally efficient coarse-grained simulation of chemical reaction (of PFPEs and other compounds) under equilibrium and nonequilibrium conditions.